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I, Neil Thomas SIMPKIN BA,

Deputy Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

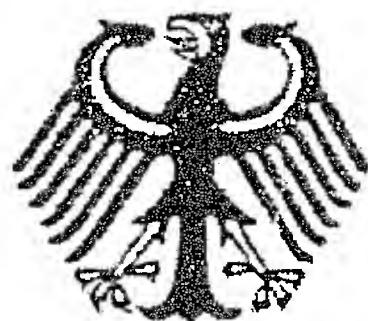
1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the German and English languages.
3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 11 June 2003 under the number 103 26 211.3 and the official certificate attached thereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group Ltd

The 23rd day of September 2009

FEDERAL REPUBLIC OF GERMANY



Priority Certificate for the filing of a Patent Application

File Reference: 103 26 211.3

Filing date: 11 June 2003

Applicant/Proprietor: Clariant GmbH, 65929 Frankfurt am Main/DE

Title: Heterocyclic colorants based on diazabenzoisoindoles

IPC: C 07 D, C 09 B

The attached documents are a correct and accurate reproduction of the original submission for this application.

Munich, 11 March 2004
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Description

Heterocyclic colorants based on diazabenzisoindoles

- 5 The present invention relates to novel organic colorants.

Within the field of color pigments there is a constant market demand for novel hues possessing high migration, light, and solvent fastnesses, good thermal stabilities, and high coloring intensity.

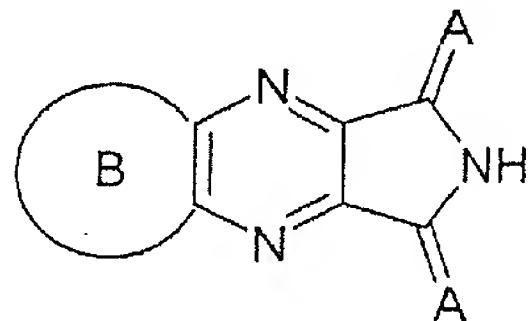
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The subject matter claimed in US 4,166,179 includes pigments deriving from 4,7-diazaisoindole, but there is no description of additional benzo-fusing on the indole framework.

- 15 The object was to find new colorants for dyeing or pigmenting organic or inorganic materials of high or low molecular weight, in particular high molecular weight organic materials, which are based on readily available intermediates.

It has been found that this object is achieved, surprisingly, by means of
20 compounds of the formula (I).

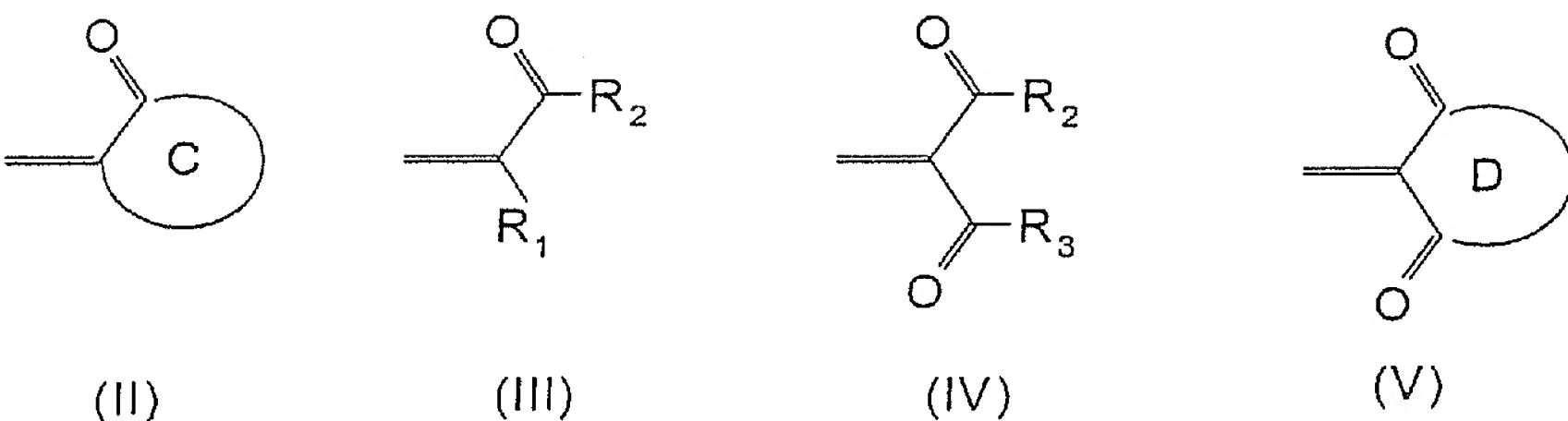
In one aspect the present invention accordingly provides compounds of the general formula (I)



(I)

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in which A is a group of the general formula (II), (III), (IV) or (V)

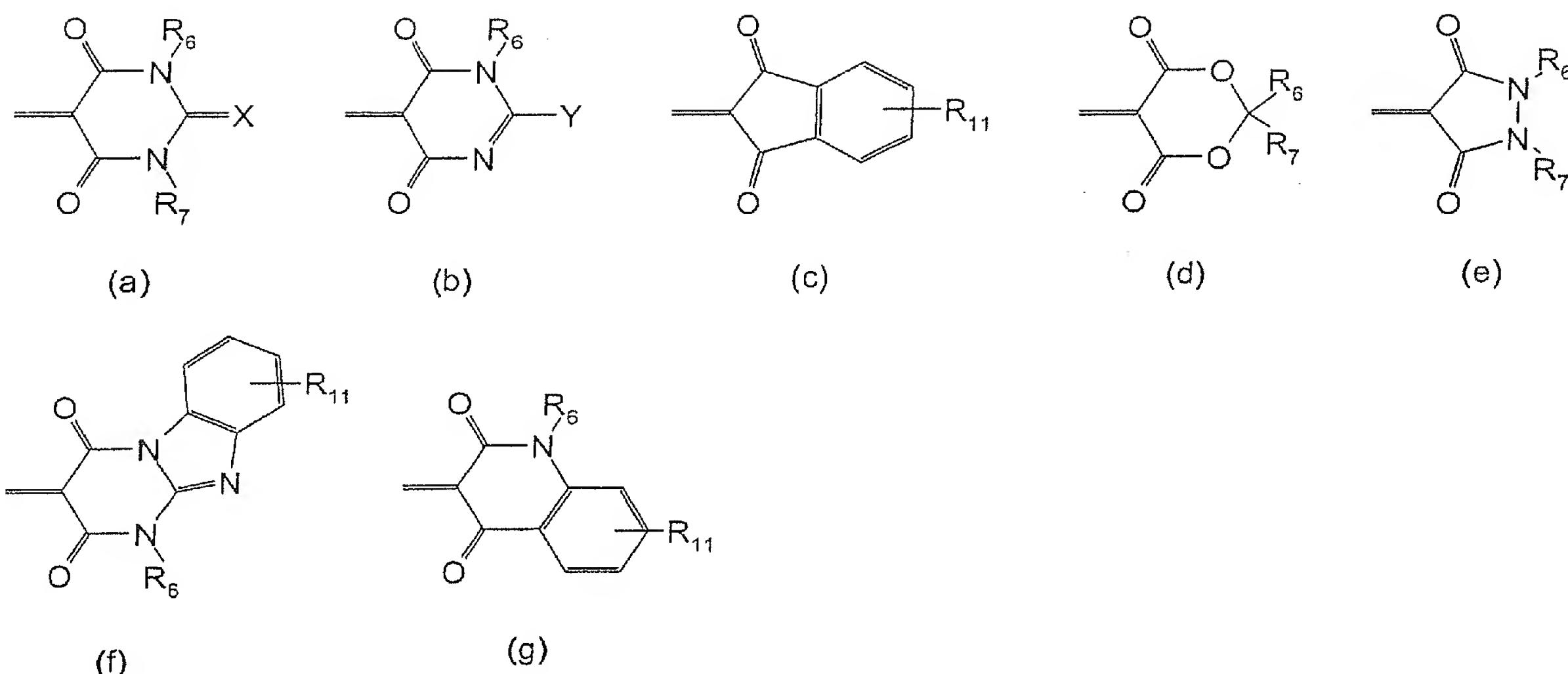


in which C and D are an alicyclic or heterocyclic group;

R₁ is CN or is a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S,

- 5 and R₂ and R₃ independently of one another are C₁-C₂₅ alkyl, C₅-C₁₂ cycloalkyl, C₆-C₂₄ aryl, OH, OR⁰ or NR₄R₅, in which R₄ and R₅ are identical or different and are hydrogen, C₁-C₂₅ alkyl, C₅-C₁₂ cycloalkyl, C₆-C₂₄ aryl which is unsubstituted or substituted by 1, 2, 3 or 4 radicals halogen, R⁰, OR⁰, SR⁰, NH₂, NHR⁰, NR⁰₂, NO₂, COOH, COOR⁰, CONH₂, CONHR⁰, CONR⁰₂, CN, SO₃H, SO₂(OR⁰), SO₂R⁰,
- 10 SO₂NHR⁰, SO₂NR⁰₂ or by a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S, or are a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S, R⁰ being C₁-C₁₈ alkyl or C₆-C₂₄ aryl;
- 15 and B is unsubstituted or mono- to tetrasubstituted ortho-C₆-C₁₈ arylene, suitable substituents being preferably halogens, R⁰, OR⁰, SR⁰, NH₂, NHR⁰, NR⁰₂, NO₂, COOH, COOR⁰, CONH₂, CONHR⁰, CONR⁰₂, CN, SO₃H, SO₂(OR⁰), SO₂R⁰, SO₂NHR⁰, SO₂NR⁰₂ or a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S.
- 20 Preference is further given to compounds of the formula (I), in which B is ortho-phenylene or 2,3-naphthylene.

Particularly preferred are compounds of the formula (I) in which A is a divalent alicyclic or heterocyclic radical of the formulae (a) to (g)



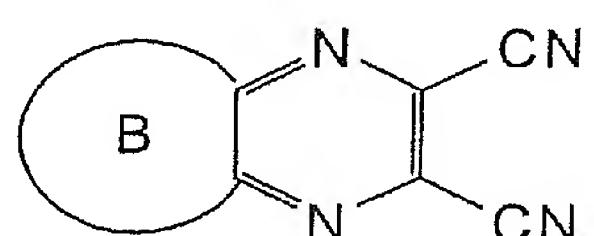
- where R₆ and R₇ independently of one another are hydrogen, C₁-C₂₅ alkyl, C₅-C₁₂ cycloalkyl, C₆-C₂₄ aryl, C₁-C₂₅ alkyl(C₆-C₁₀ aryl), a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S, -(CH₂)_n-COR₈ or -(CH₂)_m-OR₉, in which R₈ is hydroxyl, amino, unsubstituted or mono- or polyhydroxyl- or -amino-substituted C₁-C₂₅ alkoxy, C₁-C₂₅ alkylamino, di(C₁-C₂₅ alkyl)amino,
 5 C₁-C₂₅ alkyl(C₆-C₁₀ aryl)amino, (C₆-C₂₄ aryl)amino, di(C₆-C₂₄ aryl)amino, C₁-C₂₅ alkyl(C₆-C₁₀ aryl)amino, or C₂-C₂₄ alkenyloxy,
 and R₉ is hydrogen or -CO-(C₁-C₂₅ alkyl), and n and m independently of one another are an integer from 0 to 6, preferably 1 to 4, and in which in R₆, R₇, R₈, and R₉ it is also possible for a C-C unit to be replaced by an ether unit C-O-C,
 10 X is =O, =S or =NR₁₀, in which R₁₀ has one of the definitions of R₆,
 Y is hydrogen, R₇, OR₇, SR₇, NHCN or NR₇R₁₀,
 and R₁₁ is hydrogen, halogen, CN, R₇, OR₇, SR₇, NR₇R₁₀, NO₂, SO₂(OR₇), SO₂R₇,
 15 SO₂NHR₇, SO₂N(R₇)₂ or PO₂(OR₇).
 20 With particular preference R₆ and R₇ are hydrogen, C₁-C₁₈ alkyl, C₅-C₆ cycloalkyl, C₆-C₁₀ aryl, benzyl, pyridyl, pyrryl, thienyl, imidazolyl, oxazolyl, thiazolyl, pyrimidyl, hydroxycarbonyl-C₀-C₆ alkyl, C₁-C₁₈ alkoxy carbonyl-C₀-C₆ alkyl, aminocarbonyl-C₀-C₆ alkyl; C₁-C₁₈ alkylaminocarbonyl-C₀-C₆ alkyl, C₆-C₁₀ arylaminocarbonyl-C₀-C₆ alkyl, di(C₁-C₁₈ alkyl)aminocarbonyl-C₀-C₆ alkyl, C₁-C₁₈ alkyl-C₆-C₁₀ arylaminocarbonyl-C₀-C₆ alkyl and di(C₆-C₁₀ aryl)aminocarbonyl-

C₀-C₆ alkyl.

With particular preference R₈ is hydroxyl, C₁-C₁₈ alkoxy, C₁-C₁₈ alkylamino, di(C₁-C₁₈ alkyl)amino, benzylamino, C₆-C₁₀ arylamino, di(C₆-C₁₀ aryl)amino or (C₂-C₁₈)alkenyloxy.

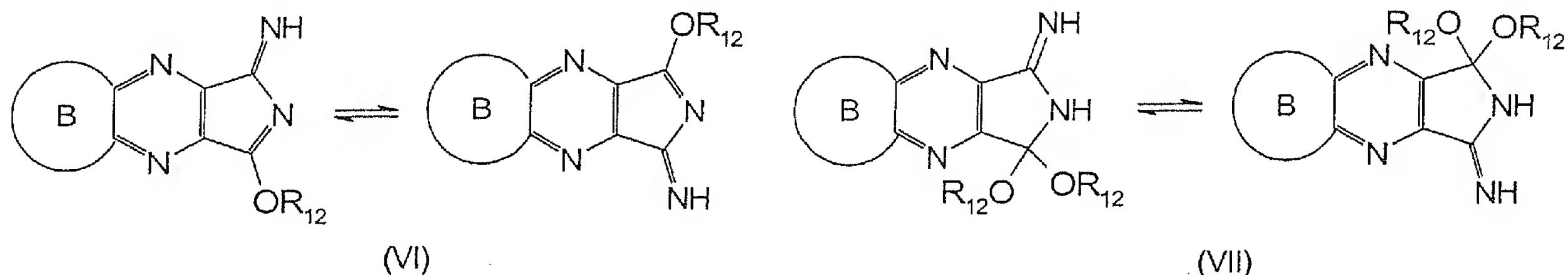
With particular preference R₁₁ is hydrogen, Cl, Br, C₁-C₁₈ alkyl, C₅-C₆ cycloalkyl, benzyl, C₆-C₁₀ aryl, pyridyl, pyrryl, thienyl, imidazolyl, oxazolyl, thiazolyl, pyrimidyl, C₁-C₁₈ alkoxy, C₆-C₁₀ aryloxy, C₁-C₁₈ alkylthio, C₆-C₁₀ arylthio, C₁-C₁₈ alkylamino, C₆-C₁₀ arylamino, di(C₁-C₁₈ alkyl)amino, C₁-C₁₈ alkyl(C₆-C₁₀ aryl)amino, di(C₆-C₁₀ aryl)amino, SO₃H, C₁-C₁₈ alkoxy sulfonyl, C₁-C₁₈ alkylsulfonyl, C₁-C₁₈ alkylaminosulfonyl and di(C₁-C₁₈ alkyl)aminosulfonyl.

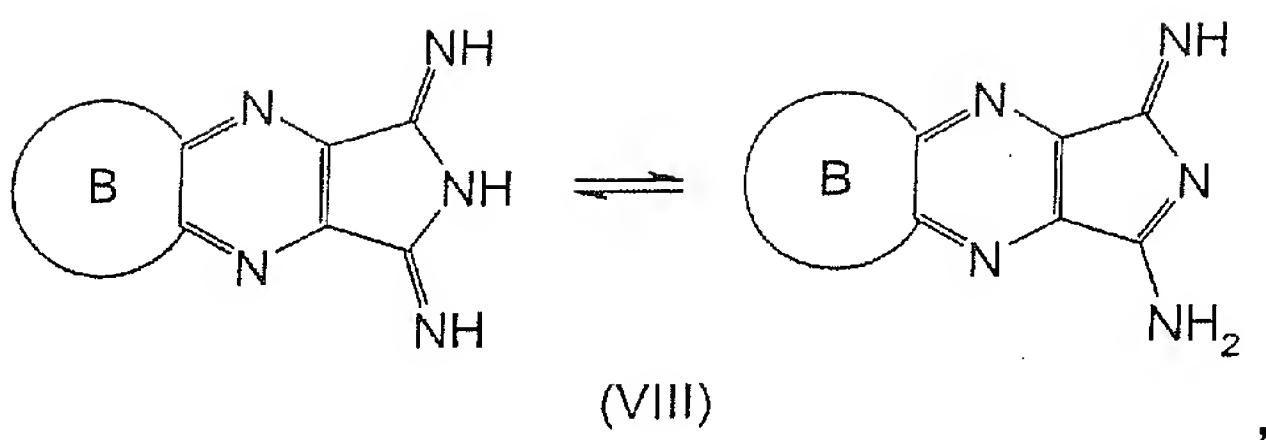
The present invention further provides a process for preparing compounds of the general formula (I) by reacting a 2,3-dicyanoquinoxaline of the formula (XIV)



(XIV)

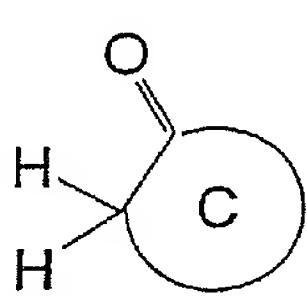
with a total of at least 2 equivalents of ammonia and/or alkoxides MOR₁₂, in which M is sodium or potassium, such as sodium methoxide, sodium ethoxide, sodium pentoxide, potassium methoxide or potassium *tert*-butoxide, to give di- or monoimino-substituted diazabenzisoindoles bearing 0 to 2 alkoxy substituents, represented for example by compounds of the formulae (VI), (VII) or (VIII),





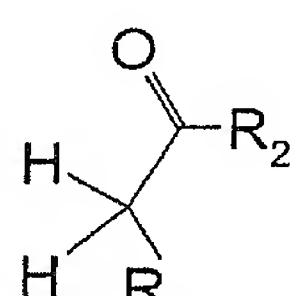
in which R₁₂ is C₁-C₁₈ alkyl or -(CH₂)_m-OH and m is an integer in the range from 1 to 6, and it is also possible for a C-C unit to be replaced by an ether unit C-O-C,

- 5 in a solvent or solvent mixture under basic to neutral conditions at a temperature of -20 to 120°C, preferably 0 to 100°C, more preferably 20 to 80°C,
 which are subsequently reacted, following isolation or without isolation, in a
 solvent or solvent mixture under neutral to acidic conditions, preferably in the
 presence of an organic acid, such as formic acid, acetic acid or propionic acid, or
 10 of an inorganic acid, such as sulfuric acid, hydrochloric acid or phosphoric acid,
 and advantageously at a temperature of 10 to 250°C, in particular 20 to 200°C,
 more preferably 30 to 150°C, with at least 2 equivalents of a compound of the
 formulae (IX), (X), (XI) or (XII)

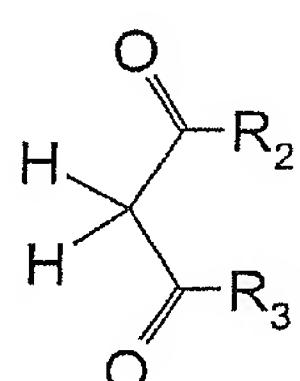


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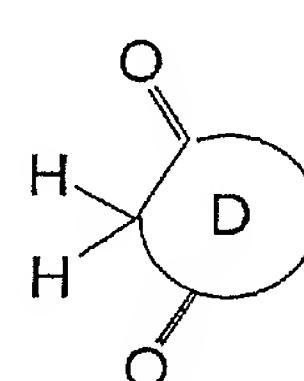
(IX)



(X)

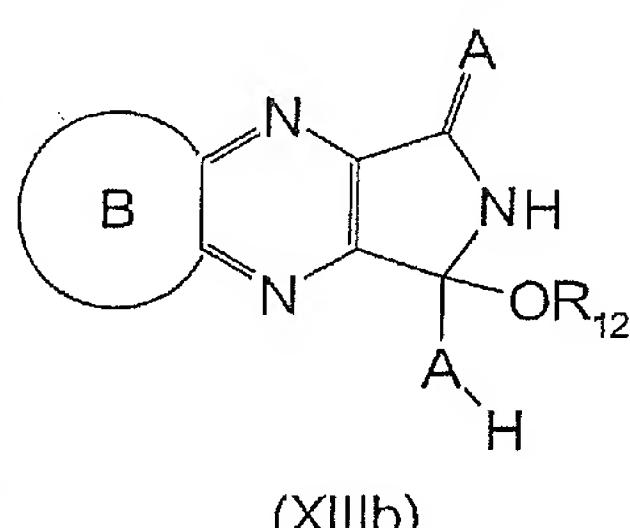
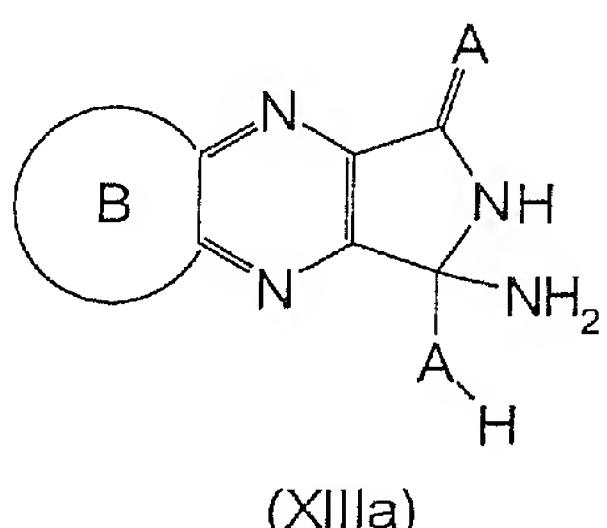


(XI)



(XII)

in which C, D, R₁, R₂, and R₃ are as defined above,
 to give a further intermediate of the general formula (XIIIa) or (XIIIb)

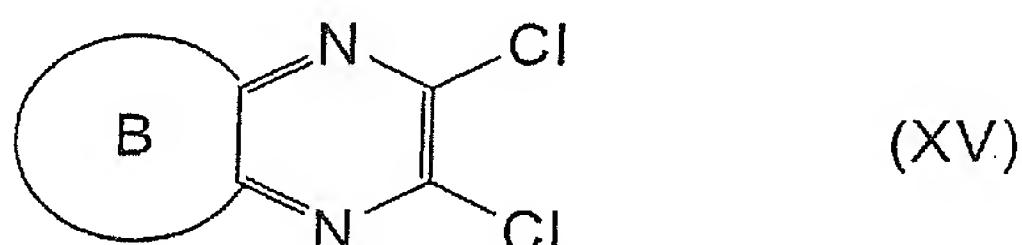


from which subsequently one mole of ammonia or HOR₁₂ is eliminated.

The elimination of ammonia and/or HOR₁₂ to give the compounds of the formula (I) according to the invention is accomplished advantageously at a temperature of 5 -30 to 250°C, preferably -20 to 200°C, more preferably 0 to 150°C, preferably in the presence of a solvent such as water, methanol, ethanol, glycols, dimethylformamide, N-methylpyrrolidone or toluene, and more preferably in the presence of an organic acid, such as formic acid, acetic acid or propionic acid, or in the presence of an inorganic acid, such as sulfuric acid, hydrochloric acid or 10 phosphoric acid.

2,3-Dicyanoquinoxalines of the formula (XIV) can be prepared in accordance with Liebigs Ann. Chem. 1981, 2, pages 333-341, by reacting corresponding 2,3-dichloroquinoxalines of the formula (XV)

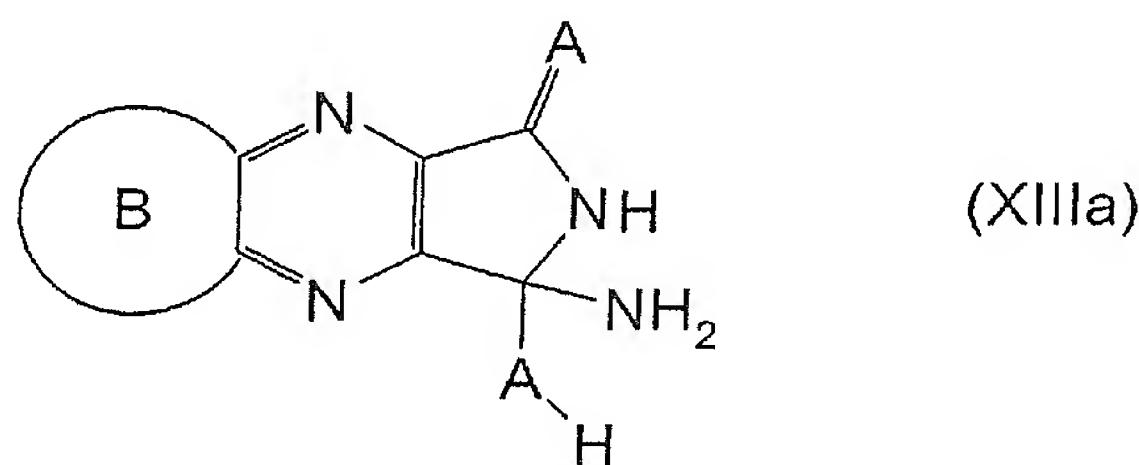
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with at least twice the molar amount of tetraethylammonium cyanide in DMSO. Surprisingly it has now been found that a cyanide of a main-group or transition-20 group metal can also be used, in an organic solvent, in the presence of a phase-transfer catalyst, at elevated temperatures. Preferred cyanides are those of an alkali metal or alkaline earth metal, CuCN, Zn(CN)₂ or Fe(CN)₂, preferably sodium cyanide. The reaction of compounds of the general formula (XV) occurs preferably 25 in an organic solvent having a high dielectric constant, such as DMSO, DMF, dimethylacetamide, NMP, acetonitrile, sulfolane, and dioxolane, preferably DMSO and NMP, in particular DMSO, in the presence of a phase-transfer catalyst selected from the group of quaternary alkylammonium salts, especially quaternary alkylammonium halides, such as distearyldimethylammonium chloride, trimethylbenzylammonium bromide or tetrabutylammonium chloride, at 30 temperatures of 0 to 150°C, in particular at 10 to 100°C, preferably at 20 to 80°C.

The advantage of the new process is that it is possible to start from the relatively inexpensive sodium cyanide, which is less hygroscopic than the organic cyanide and, furthermore, has a significantly lower toxicity, and that the phase-transfer catalyst can be used in a substoichiometric molar amount, preferably in 0.01 to 0.9 times the molar amount, based on the starting product of the formula (XV).

The present invention additionally provides an intermediate of the general formula (XIIIa),



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Compounds of the general formula (I) according to the present invention are used for dyeing or pigmenting organic or inorganic, high or low molecular weight, in particular high molecular weight organic, materials.

- 15 Depending on the identity of their substituents and of the high molecular weight organic material to be colored, the compounds of the invention can be used as polymer-soluble dyes or as pigments. In the latter case it is advantageous to convert the as-synthesized products (crude pigments) by aftertreatment in organic solvents – in which the pigments themselves are not dissolved – and at elevated 20 temperatures, for example at 60 to 200°C, in particular at 70 to 150°C and preferably at 75 to 100°C, into a finely disperse form often having further improved pigmentary properties. The aftertreatment is preferably combined with a grinding or kneading operation.
- 25 The colorants of the invention are outstandingly suitable for coloring high molecular weight materials, which may be organic or inorganic in nature, and are plastics and/or natural materials. These may be, for example, natural resins, drying oils, rubber or casein. Alternatively they may be modified natural materials, such as chlorinated rubber, oil-modified alkyd resins, viscose, cellulose

- derivatives, such as cellulose esters or cellulose ethers, and, in particular, synthetic organic polymers (plastics), which may be obtained by addition polymerization, polycondensation or polyaddition. From the class of the plastics prepared by addition polymerization mention may be made in particular of the
- 5 following: polyolefins, such as polyethylene, polypropylene, polyisobutylene, and substituted polyolefins such as polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinylacetals, polyacrylonitrile, polyacrylic acid, polymethacrylic acid, polyacrylic esters and polymethacrylic esters or polybutadiene, for example, and also copolymers thereof.
- 10 From the class of the plastics prepared by polyaddition and polycondensation mention may be made of the following: polyesters, polyamides, polyimides, polycarbonates, polyurethanes, polyethers, polyacetals, and also the condensation products of formaldehyde with phenols (phenolic resins) and the condensation products of formaldehyde with urea, thiourea, and melamine (amino
- 15 resins). The materials in question may also be silicones or silicone resins.

High molecular weight materials of this kind can be present individually or in mixtures in the form of plastic masses or melts or in the form of spinning solutions. They may also be present in the form of their monomers or in the polymerized

20 state, in dissolved form, as film formers or binders for paints or printing inks, such as linseed-oil varnish, nitrocellulose, alkyd resins, melamine resins and formaldehyde resins or acrylic resins.

The compounds of the invention are suitable, accordingly, as colorants in oil-based or water-based paints, in coating materials of various kinds, camouflage paints, for spin coloring, for the mass coloring or pigmenting of plastics, in printing inks for the graphics industry, such as, for example, in paper, textile or decorative printing, and in the mass coloring of paper, for preparing inks, water-based or non-water-based ink-jet inks, microemulsion inks, and inks which operate in accordance with the hot-melt process.

The compounds of the invention are also suitable for use as colorants in electrophotographic toners and developers, such as, for example, one- or two-component powder toners (also called one- or two-component developers), magnetic toners, liquid toners, latex toners, polymerization toners, and specialty toners.

Typical toner binders are addition polymerization resins, polyaddition resins, and polycondensation resins, such as styrene, styrene-acrylate, styrene-butadiene, acrylate, polyester, phenol-epoxy resins, polysulfones, polyurethanes, individually or in combination, and also polyethylene and polypropylene, which may include further ingredients, such as charge control agents, waxes or flow assistants, or are modified subsequently with these additions.

The compounds of the invention are additionally suitable for use as colorants in powders and powder coating materials, particularly in triboelectrically or electrokinetically sprayable powder coating materials which are employed to coat the surfaces of articles made, for example, of metal, wood, plastic, glass, ceramic, concrete, textile material, paper or rubber.

Typical powder coating resins used include epoxy resins, carboxyl- and hydroxyl-containing polyester resins, polyurethane resins, and acrylic resins, together with customary hardeners. Resin combinations are also used. Thus, for example, epoxy resins are frequently used in combination with carboxyl- and hydroxyl-containing polyester resins. Typical hardener components (depending on the resin system) are, for example, acid anhydrides, imidazoles and also dicyandiamide and their derivatives, blocked isocyanates, bisacylurethanes, phenolic resins, melamine resins, triglycidyl isocyanurates, oxazolines, and dicarboxylic acids.

Additionally the compounds of the invention are suitable for use as colorants in inks, preferably ink-jet inks, for example water-based or nonwater-based ink-jet inks, microemulsion inks and also in those inks which operate in accordance with the hot-melt process.

Ink-jet inks contain in general a total of 0.5% to 15%, preferably 1.5% to 8%, by weight (calculated on a dry basis) of one or more of the compounds of the invention.

Microemulsion inks are based on organic solvents, water and, if desired, an additional hydrotropic substance (interface mediator).

Microemulsion inks contain 0.5% to 15%, preferably 1.5% to 8%, by weight of one or more of the compounds of the invention, 5% to 99% by weight of water and 0.5% to 94.5% by weight of organic solvent and/or hydrotropic compound.

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Solvent-based ink-jet inks contain preferably 0.5% to 15% by weight of one or more of the compounds of the invention, 85% to 99.5% by weight of organic solvent and/or hydrotropic compounds.

Hot-melt inks are based mostly on waxes, fatty acids, fatty alcohols or sulfonamides which are solid at room temperature and liquefy on heating, the preferred melting range being situated between about 60°C and about 140°C. Hot-melt ink-jet inks are composed, for example, essentially of 20% to 90% by weight of wax and 1% to 10% by weight of one or more of the compounds of the invention. Additionally there may be 0% to 20% by weight of an additional polymer (as "dye dissolver"), 0% to 5% by weight of dispersing assistants, 0% to 20% by weight of viscosity modifiers, 0% to 20% by weight of plasticizers, 0% to 10% by weight of tack additive, 0% to 10% by weight of transparency stabilizer (which prevents, for example, the waxes crystallizing) and 0% to 2% by weight of antioxidant.

The compounds of the invention are also suitable, moreover, for use as colorants for color filters, both for additive and for subtractive color generation, and also as colorants for electronic inks ("e-inks") or electronic paper ("e-paper"); the latter are described for example in S. Maeda, K. Gocho, M. Omadani, "Electrical Twisting Sticks in a Transparent Tube", Proceedings of the International Congress of Imaging Science 2002, Tokyo May 13-17, 2002, pages 507-508.

The compounds of the invention are, furthermore, suitable for use as colorants in cosmetics, for coloring seed, and for coloring mineral oils, lubricating greases, and waxes.

Depending on the nature of the substituents of the compounds of the invention the colorations obtained are distinguished by good heat fastness, light fastness and weather fastness, by chemical resistance and by the very good applications properties, e.g., crystallization fastness and dispersion fastness, and in particular by their migration fastness, bleed fastness, fastness to overcoating, and solvent fastness. The compounds used as polymer-soluble dyes naturally have only little, or restricted, solvent fastness.

The invention additionally provides a composition comprising an organic or inorganic, high or low molecular weight material, particularly high molecular weight organic material, and at least one compound of the invention in a coloristically effective amount, generally in the range from 0.005% to 70% by weight, in particular from 0.01% to 10% by weight, based on the organic or inorganic material.

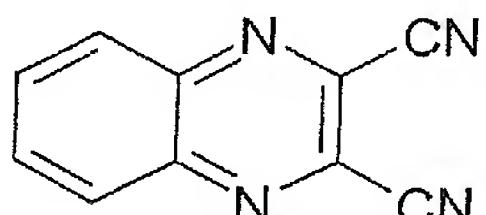
Examples

Intermediates

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Example A: 2,3-Dicyanoquinoxaline

A mixture of 10.0 g of 2,3-dichloroquinoxaline, 5.40 g of sodium cyanide and 9.32 g of benzyltrimethylammonium chloride is stirred in 500 ml of DMSO at room temperature for 17 hours. With intensive stirring the reaction mixture is poured onto 1000 ml of ice-water, stirred for an hour, and filtered with suction, and the solid product is washed with water. Drying at 60°C gives 8.03 g (89% of theory) of pale gray crystals with the following formula

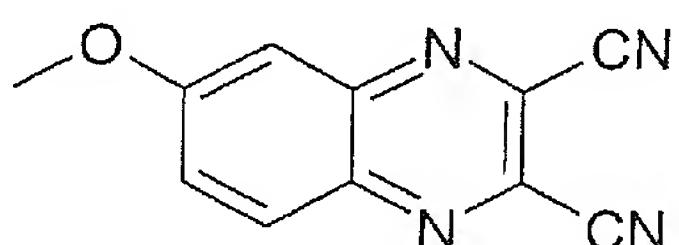


MS (m/e): 181 [M+H]⁺, 203 [M+Na]⁺

15 H NMR (DMSO): 8.34 (m, 2H), 8.23 (m, 2H)

Example B: 2,3-Dicyano-6-methoxyquinoxaline

A mixture of 31.1 g of 2,3-dichloro-6-methoxyquinoxaline, 14.7 g of sodium cyanide and 2.79 g of benzyltrimethylammonium chloride is stirred in 210 ml of DMSO at room temperature for 48 hours. With intensive stirring the reaction mixture is poured onto 520 ml of ice-water, stirred for an hour, and filtered with suction, and the solid product is washed with water. Drying at 40°C gives 23.8 g (83% of theory) of pale gray crystals with the following formula



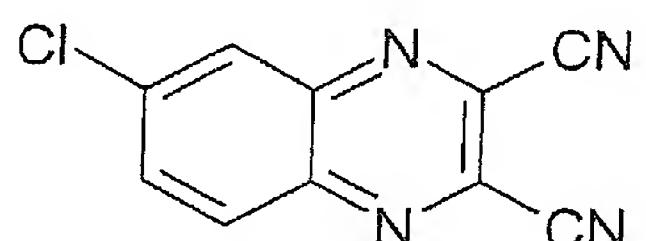
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MS (m/e): 211 [M+H]⁺, 233 [M+Na]⁺

H NMR (DMSO): 8.21 (d, 1H), 7.83 (dd, 1H), 7.68 (d, 1H), 4.02 (s, 3H)

Example C: 6-Chloro-2,3-dicyanoquinoxaline

A mixture of 11.7 g of 2,3,6-trichloroquinoxaline, 5.39 g of sodium cyanide and 2.04 g of benzyltrimethylammonium chloride is stirred in 200 ml of DMSO at room temperature for 24 hours. With intensive stirring the reaction mixture is poured onto 520 ml of ice-water, stirred for an hour, and filtered with suction, and the solid product is washed with water. Drying at 40°C gives 8.12 g (76% of theory) of a gray powder of a compound with the following formula



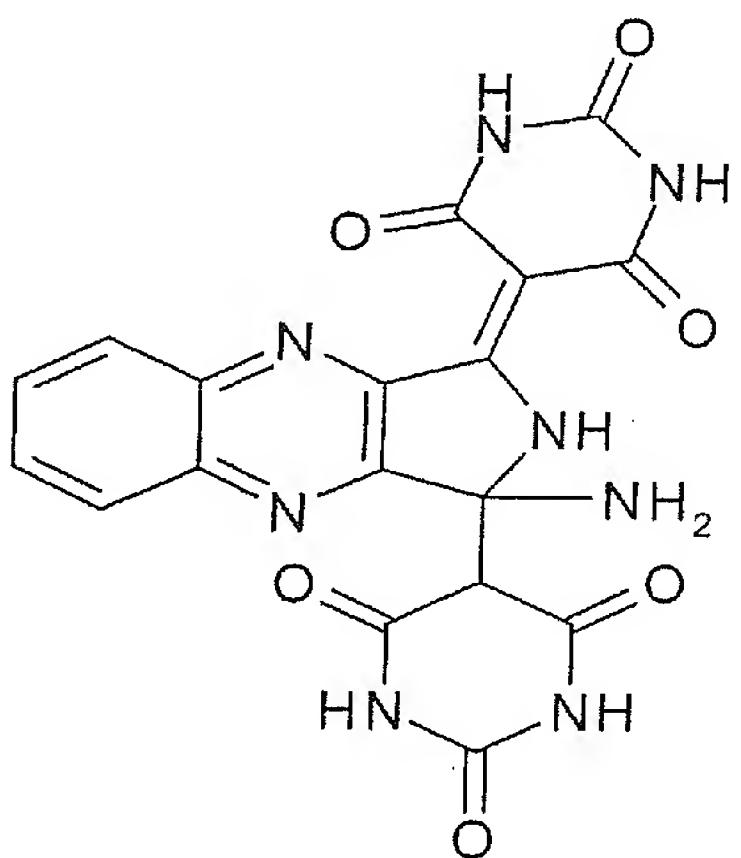
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MS (m/e): 215 [M+H]⁺, 237 [M+Na]⁺

H NMR (DMSO): 8.53 (d, 1H), 8.37 (d, 1H), 8.26 (dd, 1H)

Example D: 1-Amino-1-(2,4,6-trioxotetrahydropyrimidin-5-yl)-3-(2,4,6-trioxo-tetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole

A suspension of 175 g of 2,3-dicyanoquinoxaline in 1700 ml of methanol is admixed dropwise at 10°C with 23.0 g of sodium methoxide solution (30% in methanol) and stirred at room temperature for 16 hours. The mixture is diluted with 3500 ml of methanol and, following addition of 52.2 g of glacial acetic acid and 261 g of barbituric acid, is stirred at reflux for 6 hours. After cooling to room temperature the suspension is filtered and the solid product is washed with methanol and then with water and dried at 60°C. This gives 154 g (84% of theory) of a light brown powder of the following formula



Melting point: >300°C

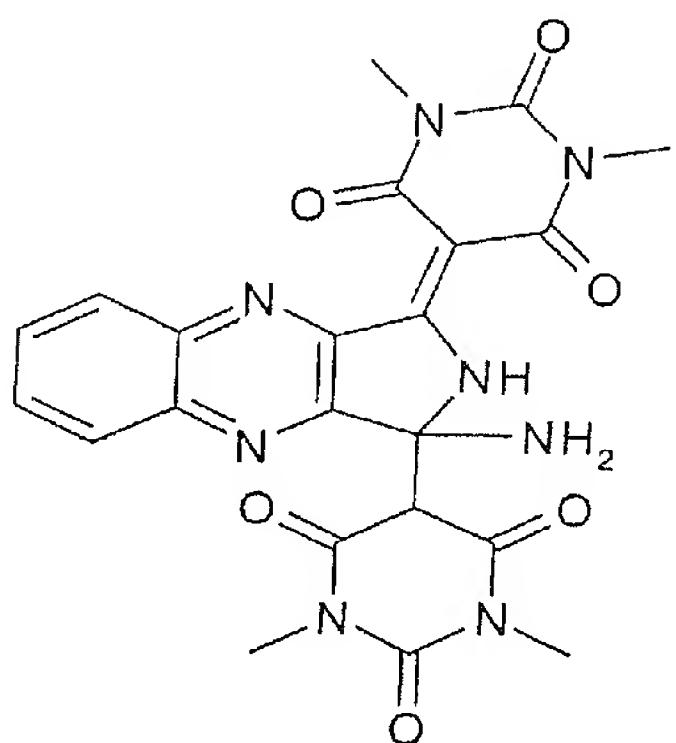
MS (m/e): 437 [M+H]⁺, 459 [M+Na]⁺

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Example E: 1-Amino-1-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5-yl)-3-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole

A suspension of 22.8 g of 2,3-dicyanoquinoxaline in 180 ml of methanol is admixed dropwise at 10°C with 3.0 g of sodium methoxide solution (30% in methanol) and stirred at room temperature for 16 h. The mixture is diluted with 200 ml of methanol and, following addition of 6.8 g of glacial acetic acid and 41.6 g of 1,3-dimethylbarbituric acid, is stirred at reflux for 6 hours. After cooling to room temperature the suspension is filtered and the solid product is washed with

methanol and then with water and dried at 60°C. This gives 33.3 g (54% of theory) of a beige-brown powder of the following formula



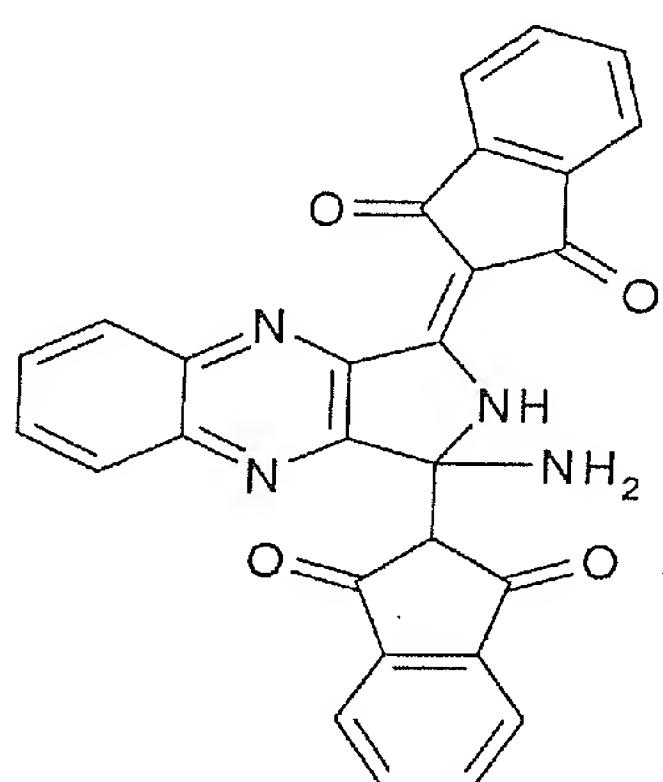
5

Melting point: >300°C

MS (m/e): 493 [M+H]⁺, 515 [M+Na]⁺

Example F: 1-Amino-1-(1,3-dioxoindan-2-yl)-3-(1,3-dioxoindan-2-ylidene)-4,9-
10 diazabenzof[f]isoindole

A suspension of 17.5 g of 2,3-dicyanoquinoxaline in 170 ml of methanol is admixed dropwise at 10°C with 2.3 g of sodium methoxide solution (30% in methanol) and stirred at room temperature for 16 hours. The mixture is diluted with 360 ml of methanol and, following addition of 5.2 g of glacial acetic acid and 15 29.8 g of 1,3-dioxoindane, is stirred at reflux for 6 hours. After cooling to room temperature the suspension is filtered and the solid product is washed with methanol and then with water and dried at 60°C. This gives 31.5 g (69% of theory) of a brown powder of the following formula



Melting point: >300°C

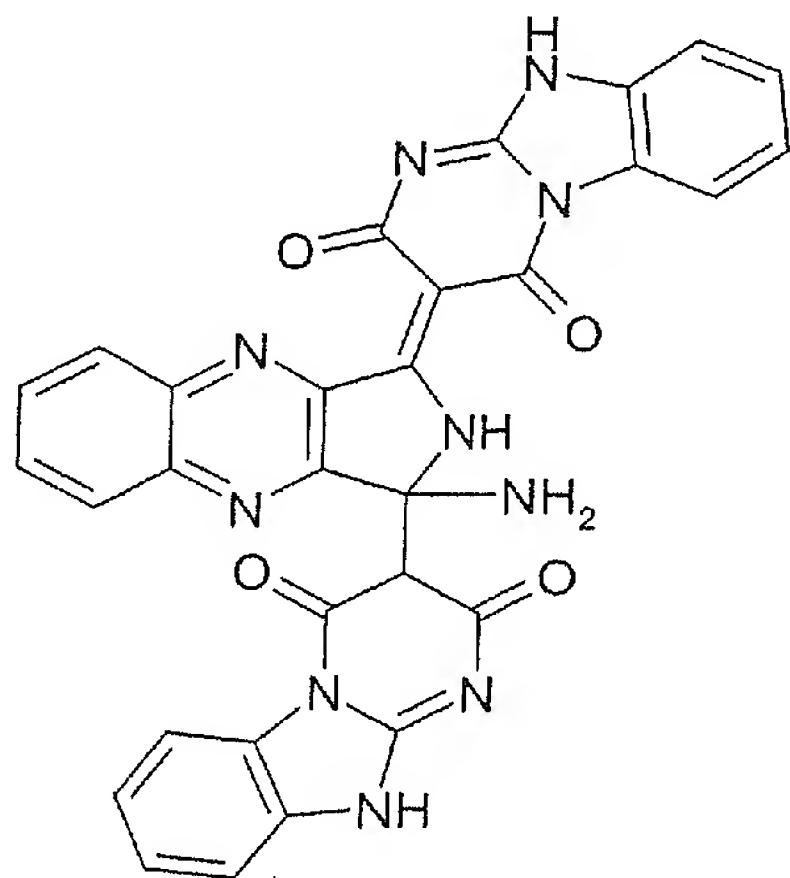
MS (m/e): 473 [M+H]⁺, 495 [M+Na]⁺

Example G: 1-Amino-1-(2,4-dioxo-10H-benzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)-3-

5 (2,4-dioxo-10H-benzo[4,5]imidazo[1,2-a]pyrimidin-3-ylidene)-4,9-diazabenzofisoindole

A suspension of 10.0 g of 2,3-dicyanoquinoxaline in 100 ml of methanol is admixed dropwise at 10°C with 1.1 g of sodium methoxide solution (30% in methanol) and stirred at room temperature for 16 hours. The mixture is diluted 10 with 200 ml of methanol and, following addition of 2.5 g of glacial acetic acid and 23.5 g of 1H-benzo[4,5]imidazo[1,2-a]pyrimidine-2,4-dione, is stirred at reflux for 6 hours. After cooling to room temperature the suspension is filtered and the solid product is washed with methanol and then with water and dried at 60°C. This gives 25.9 g (80% of theory) of a light brown powder of the following formula

15



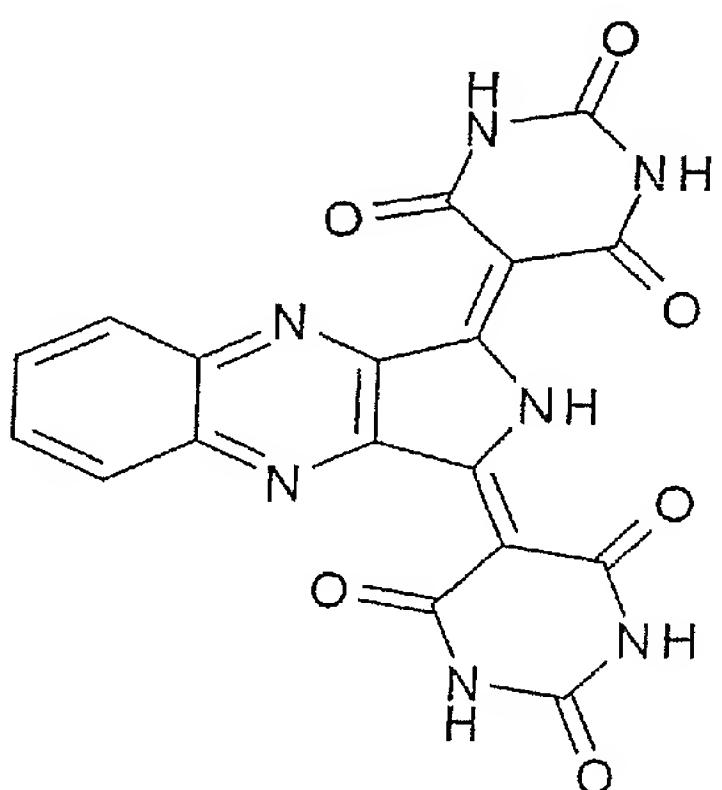
Melting point: >300°C

MS (m/e): 583 [M+H]⁺, 605 [M+Na]⁺

Colorants

Example 1: 1,3-Bis(2,4,6-trioxotetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole

5 137 g of 1-amino-1-(2,4,6-trioxotetrahydropyrimidin-5-yl)-3-(2,4,6-trioxo-tetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole are stirred in 2060 ml of sulfuric acid (80%) at room temperature for 30 minutes. Over the course of 15 minutes and at a uniform rate this solution is added dropwise with stirring to 4900 ml of water (20°C) and left to stand for a further 30 minutes. The suspension
 10 is filtered and the solid product is washed to neutrality with water and dried at 60°C. This gives 129 g (98% of theory) of a yellow compound of the following formula



15

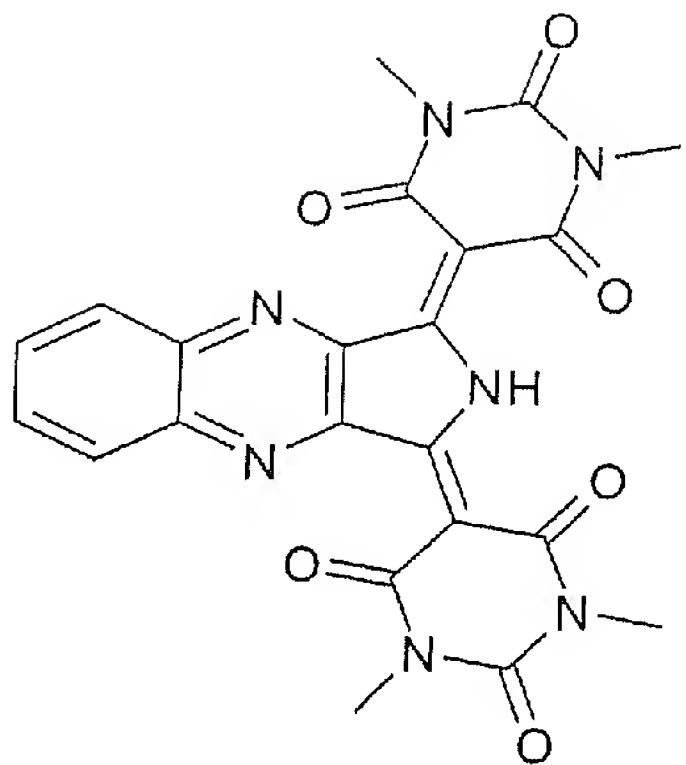
Melting point: >300°C

MS (m/e): 420 [M+H]⁺, 442 [M+Na]⁺

Example 2: 1,3-Bis(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole
 20

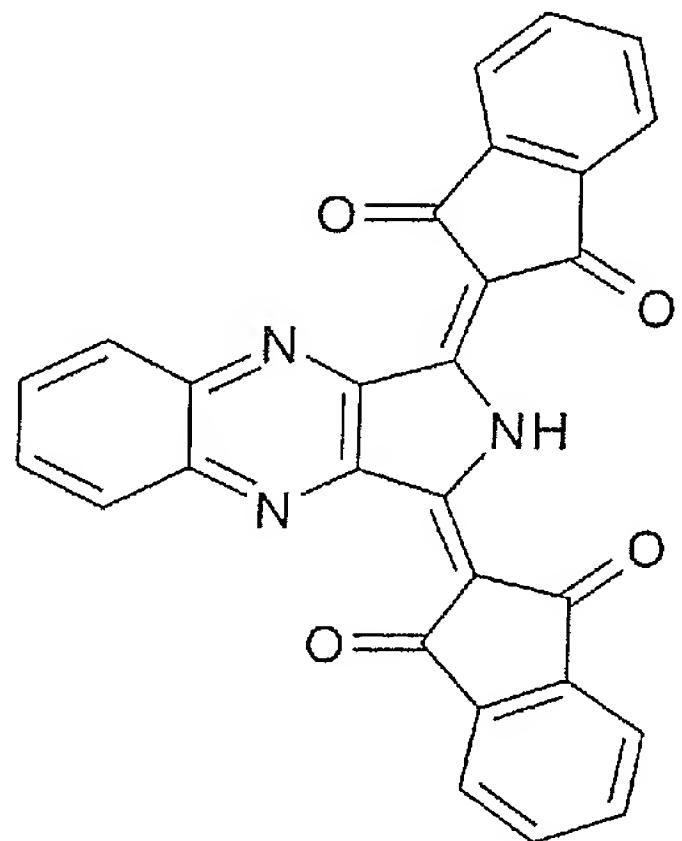
24 g of 1-amino-1-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5-yl)-3-(1,3-dimethyl-2,4,6-trioxo-tetrahydropyrimidin-5-ylidene)-4,9-diazabenzof[f]isoindole are stirred in 480 ml of concentrated sulfuric acid at room temperature for 30 minutes. Over the course of 15 minutes and at a uniform rate this solution is added
 25 dropwise with stirring to 4800 ml of water and left to stand for a further 30 minutes. The suspension is filtered and the solid product is washed to neutrality with water

and dried at 60°C. This gives 16.7 g (72% of theory) of a yellow compound of the following formula



- 5 Melting point: >300°C
MS (m/e): 476 [M+H]⁺, 498 [M+Na]⁺

Example 3: 1,3-Bis(1,3-dioxoindan-2-ylidene)-4,9-diazabenzof[f]isoindole
5.0 g of 1-amino-1-(1,3-dioxoindan-2-yl)-3-(1,3-dioxoindan-2-ylidene)-4,9-
10 diazabenzof[f]isoindole are stirred in 75 ml of concentrated sulfuric acid at room
temperature for 30 minutes. Over the course of 15 minutes and at a uniform rate
this solution is added dropwise with stirring to 180 ml of water and left to stand for
a further 30 minutes. The suspension is filtered and the solid product is washed to
15 neutrality with water and dried at 60°C. This gives 4.49 g (93% of theory) of a
reddish yellow compound of the following formula

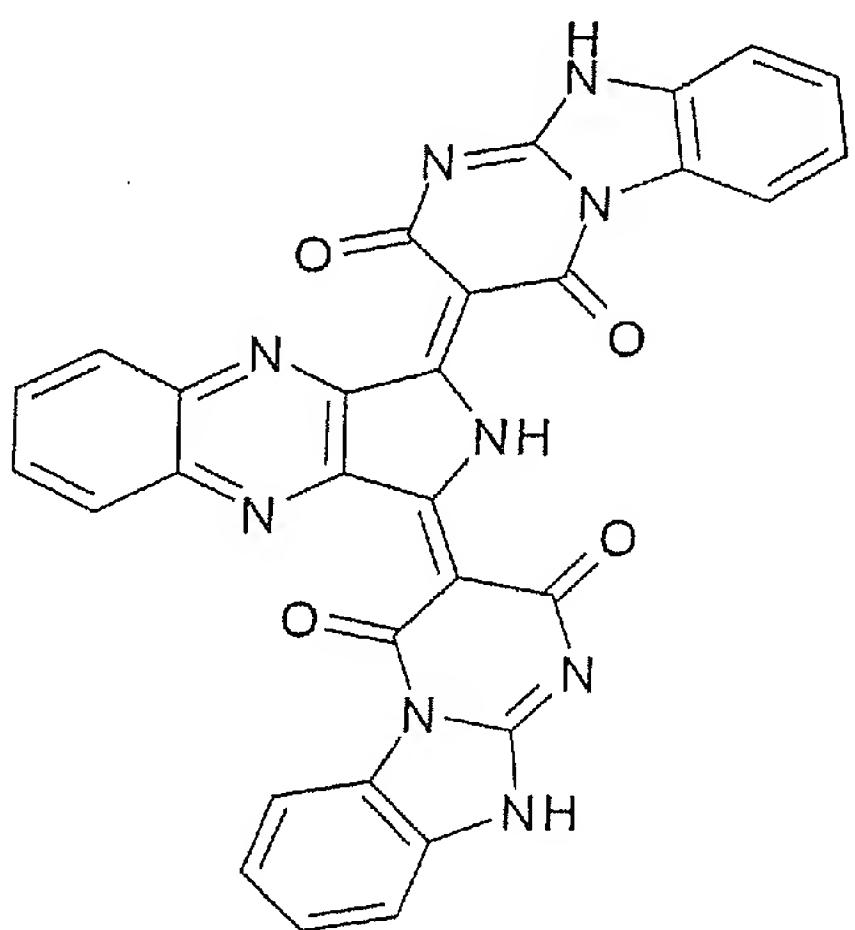


Melting point: >300°C

MS (m/e): 476 [M+H]⁺, 498 [M+Na]⁺

Example 4: 1,3-Bis(2,4-dioxo-10H-benzo[4,5]imidazo[1,2-a]pyrimidin-3-ylidene)-4,9-diazabenzof[f]isoindole

5 5.0 g of 1-amino-1-(2,4-dioxo-10H-benzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)-3-(2,4-dioxo-10H-benzo[4,5]imidazo[1,2-a]pyrimidin-3-ylidene)-4,9-diazabenzof[f]isoindole are stirred in 75 ml of concentrated sulfuric acid at room temperature for 30 minutes. Over the course of 15 minutes and at a uniform rate this solution is added dropwise with stirring to 180 ml of water and left to stand for a further 30
10 minutes. The suspension is filtered and the solid product is washed to neutrality with water and dried at 60°C. This gives 4.14 g (85% of theory) of a yellowish brown compound of the following formula



15

Melting point: >300°C

MS (m/e): 566 [M+H]⁺, 588 [M+Na]⁺

Application Examples

20

To assess the properties of the inventively prepared pigments in the coatings sector a selection was made, from among the multiplicity of known varnishes, of an aromatics-containing alkyd-melamine resin varnish (AM) based on a medium-oil alkyd resin and on a butanol-etherified melamine resin, and also of an

aromatics-free, air-drying alkyd resin varnish (LA) based on a long-oil soya alkyd resin.

Application Example 1:

- 5 Application of the pigment from Example 1 in AM varnish produces strong greenish yellow coatings in the masstone and in the white reduction.

Application Example 2:

- Application of the pigment from Example 2 in LA varnish produces strong reddish
10 yellow coatings in the masstone and in the white reduction.

Application Example 3:

- Application of the pigment from Example 3 in LA varnish produces strong reddish yellow coatings in the masstone and in the white reduction.

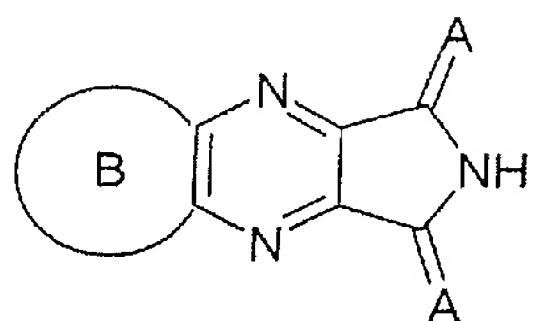
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Application Example 4:

- Application of the pigment from Example 4 in LA varnish produces reddish yellow coatings in the masstone and in the white reduction.

Claims:

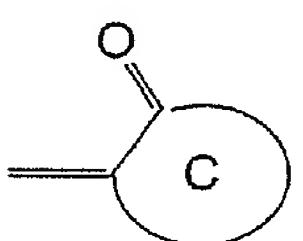
1. A compound of the general formula (I)



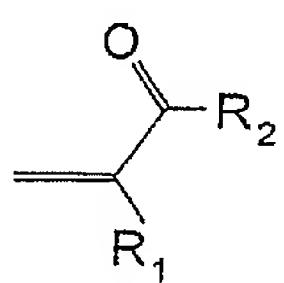
(I)

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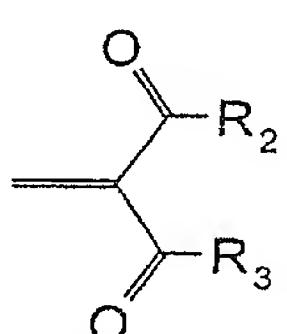
in which A is a group of the general formula (II), (III), (IV) or (V)



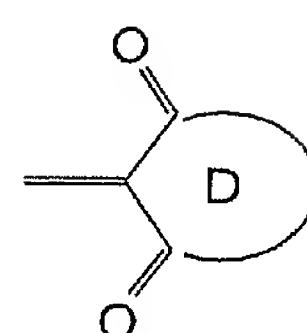
(II)



(III)



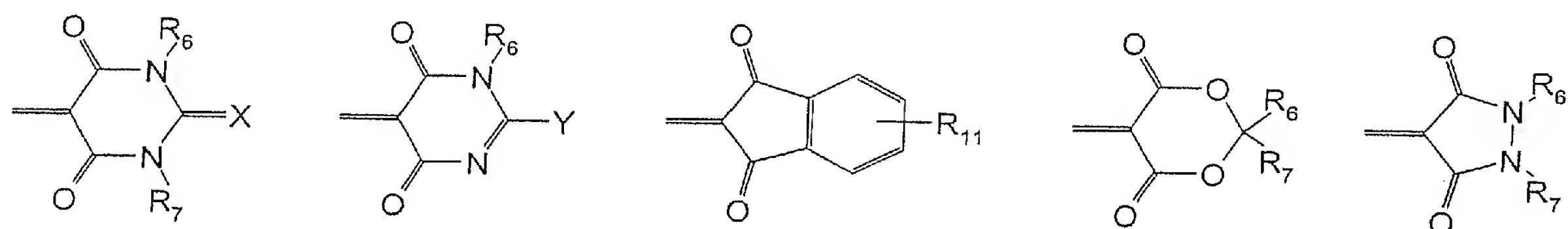
(IV)



(V)

- 10 in which C and D are an alicyclic or heterocyclic group;
 R_1 is CN or is a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S,
and R_2 and R_3 independently of one another are $\text{C}_1\text{-C}_{25}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl,
 $\text{C}_6\text{-C}_{24}$ aryl, OH, OR₄ or NR₄R₅, in which R₄ and R₅ are identical or different and
15 are hydrogen, $\text{C}_1\text{-C}_{25}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_6\text{-C}_{24}$ aryl which is unsubstituted or
substituted by 1, 2, 3 or 4 radicals halogen, R⁰, OR⁰, SR⁰, NH₂, NHR⁰, NR⁰₂, NO₂,
COOH, COOR⁰, CONH₂, CONHR⁰, CONR⁰₂, CN, SO₃H, SO₂(OR⁰), SO₂R⁰,
SO₂NHR⁰, SO₂NR⁰₂ or by a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S, or are a 5- to 7-membered
20 heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S,
R⁰ being $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_6\text{-C}_{24}$ aryl;
and B is unsubstituted or mono- to tetrasubstituted ortho-C₆-C₁₈ arylene.

2. A compound as claimed in claim 1, in which A is a divalent alicyclic or heterocyclic radical of the formulae (a) to (g)



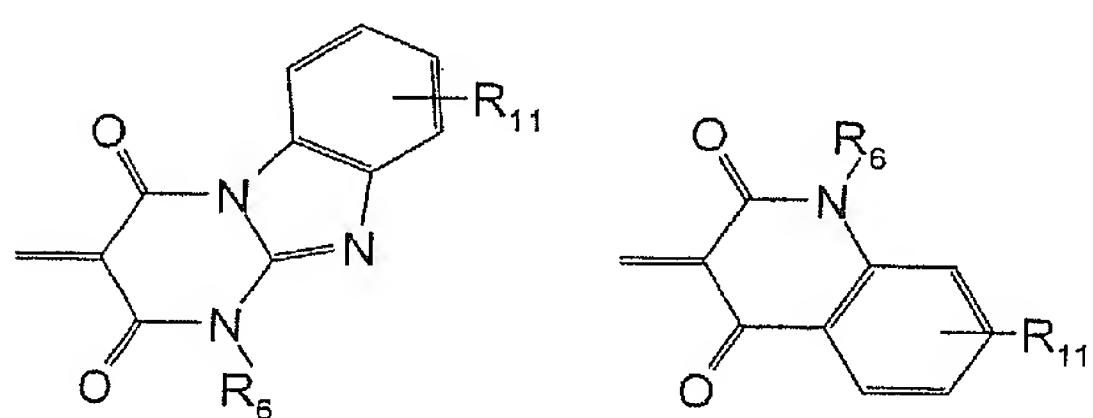
(a)

(b)

(c)

(d)

(e)



5

(f)

(g)

where R₆ and R₇ independently of one another are hydrogen, C₁-C₂₅ alkyl, C₅-C₁₂ cycloalkyl, C₆-C₂₄ aryl, C₁-C₂₅ alkyl(C₆-C₁₀ aryl), a 5- to 7-membered heteroaromatic radical having 1, 2 or 3 heteroatoms from the group N, O, and S, -(CH₂)_n-COR₈ or -(CH₂)_m-OR₉, in which R₈ is hydroxyl, amino, unsubstituted or mono- or polyhydroxyl- or -amino-substituted C₁-C₂₅ alkoxy, C₁-C₂₅ alkylamino, di(C₁-C₂₅ alkyl)amino, C₁-C₂₅ alkyl(C₆-C₁₀ aryl)amino, (C₆-C₂₄ aryl)amino, di(C₆-C₂₄ aryl)amino, C₁-C₂₅ alkyl(C₆-C₁₀ aryl)amino, or C₂-C₂₄ alkenyloxy, and R₉ is hydrogen or -CO-(C₁-C₂₅ alkyl), and n and m independently of one another are an integer from 0 to 6, and in which in R₆, R₇, R₈, and R₉ it is also possible for a C-C unit to be replaced by an ether unit C-O-C, X is =O, =S or =NR₁₀, in which R₁₀ has one of the definitions of R₆, Y is hydrogen, R₇, OR₇, SR₇, NHCN or NR₇R₁₀, and R₁₁ is hydrogen, halogen, CN, R₇, OR₇, SR₇, NR₇R₁₀, NO₂, SO₂(OR₇), SO₂R₇, 20 SO₂NHR₇, SO₂N(R₇)₂ or PO₂(OR₇).

3. A compound as claimed in claim 1 or 2, in which R₆ and R₇ are hydrogen, C₁-C₁₈ alkyl, C₅-C₆ cycloalkyl, C₆-C₁₀ aryl, benzyl, pyridyl, pyrryl, thienyl, imidazolyl, oxazolyl, thiazolyl, pyrimidyl, hydroxycarbonyl-C₀-C₆ alkyl, C₁-C₁₈ alkoxy carbonyl-C₀-C₆ alkyl, aminocarbonyl-C₀-C₆ alkyl, C₁-C₁₈ alkylaminocarbonyl-C₀-C₆ alkyl, C₆-

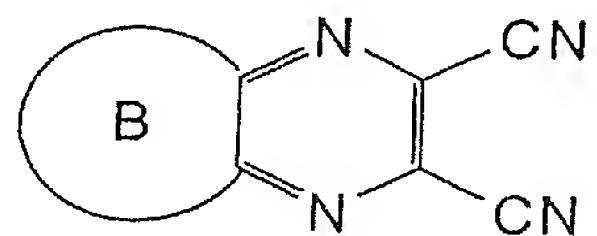
C_{10} arylaminocarbonyl- C_0 - C_6 alkyl, di(C_1 - C_{18} alkyl)aminocarbonyl- C_0 - C_6 alkyl, C_1 - C_{18} alkyl- C_6 - C_{10} arylaminocarbonyl- C_0 - C_6 alkyl or di(C_6 - C_{10} aryl)aminocarbonyl- C_0 - C_6 alkyl.

5 4. A compound as claimed in claim 2, in which R_8 is hydroxyl, C_1 - C_{18} alkoxy, C_1 - C_{18} alkylamino, di(C_1 - C_{18} alkyl)amino, benzylamino, C_6 - C_{10} arylamino, di(C_6 - C_{10} aryl)amino or (C_2 - C_{18}) alkenyloxy.

10 5. A compound as claimed in claim 2, in which R_{11} is hydrogen, Cl, Br, C_1 - C_{18} alkyl, C_5 - C_6 cycloalkyl, benzyl, C_6 - C_{10} aryl, pyridyl, pyrryl, thienyl, imidazolyl, oxazolyl, thiazolyl, pyrimidyl, C_1 - C_{18} alkoxy, C_6 - C_{10} aryloxy, C_1 - C_{18} alkylthio, C_6 - C_{10} arylthio, C_1 - C_{18} alkylamino, C_6 - C_{10} arylamino, di(C_1 - C_{18} alkyl)amino, C_1 - C_{18} alkyl(C_6 - C_{10} aryl)amino, di(C_6 - C_{10} aryl)amino, SO_3H , C_1 - C_{18} alkoxy sulfonyl, C_1 - C_{18} alkylsulfonyl, C_1 - C_{18} alkylaminosulfonyl or di(C_1 - C_{18} alkyl)aminosulfonyl.

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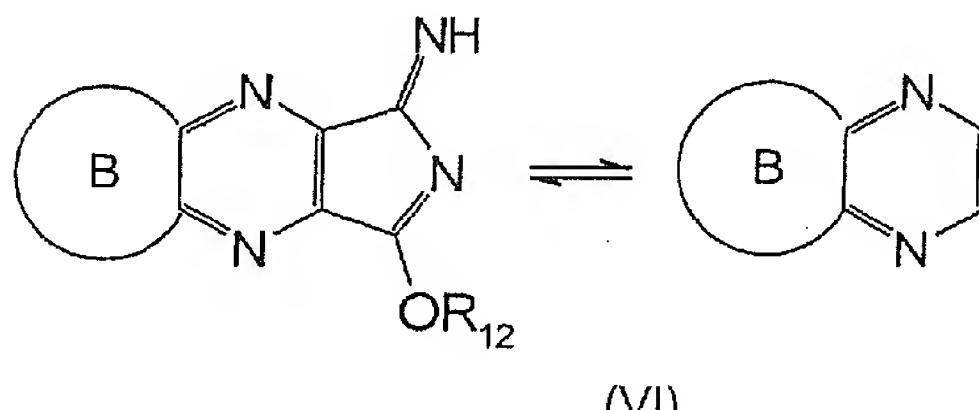
6. A process for preparing a compound as claimed in one or more of claims 1 to 5, by reacting a 2,3-dicyanoquinoxaline of the formula (XIV)



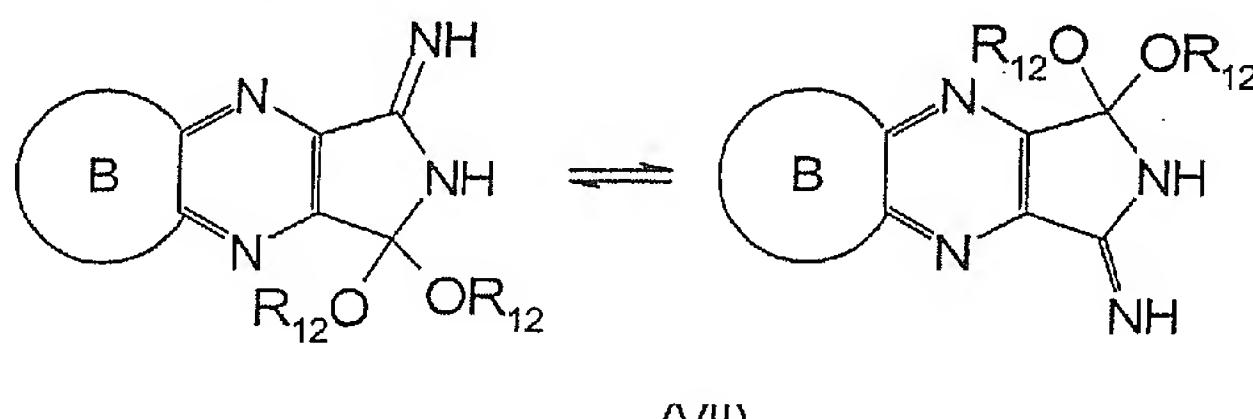
(XIV)

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with a total of at least 2 equivalents of ammonia and/or alkoxides MOR_{12} , in which M is sodium or potassium, to give di- or monoimino-substituted diazabenzisoindoles of the formulae (VI), (VII) or (VIII)

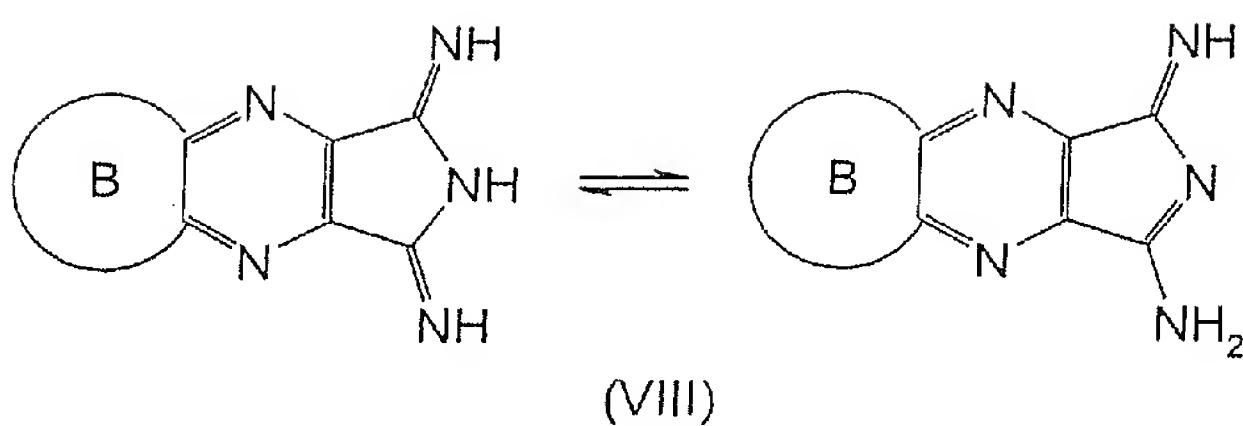


(VI)



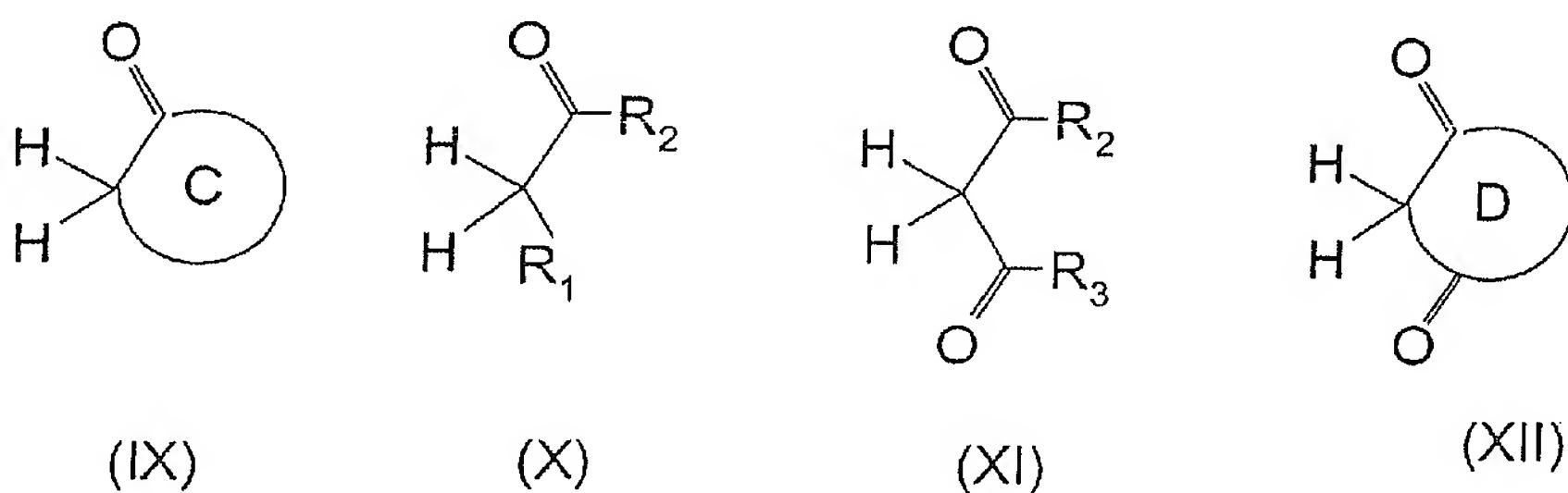
(VII)

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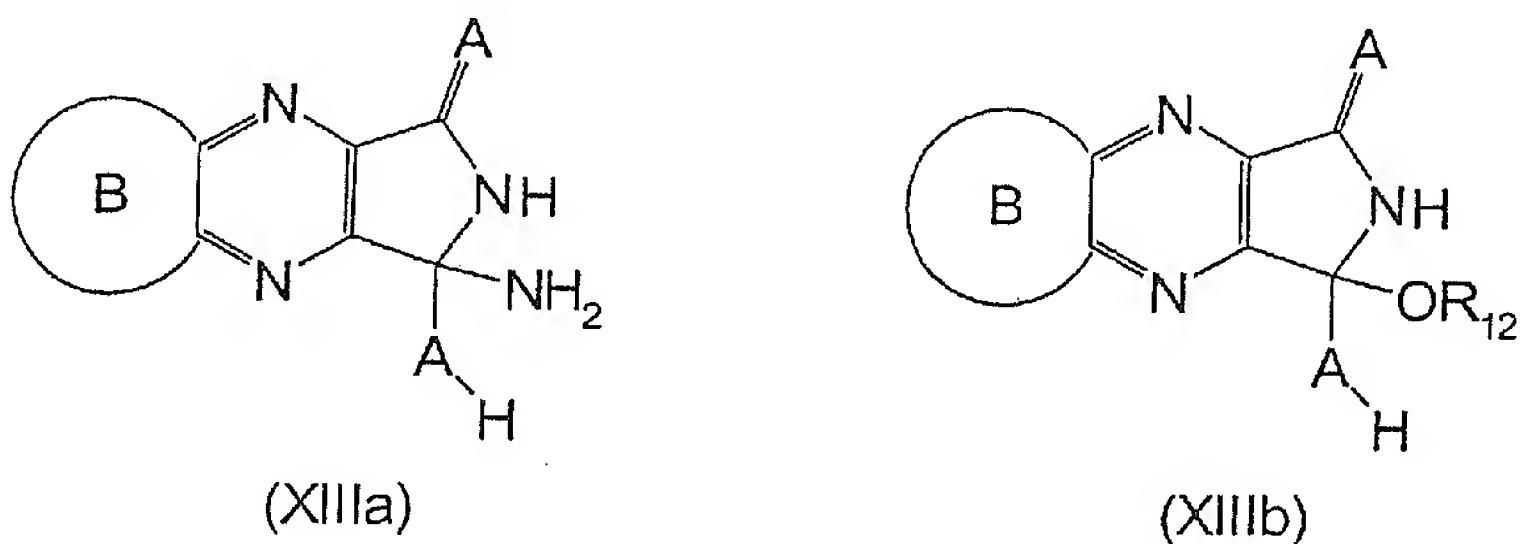


in which R_{12} is C_1-C_{18} alkyl or $-(CH_2)_m-OH$ and m is an integer in the range from 1 to 6, and it is also possible for a C-C unit to be replaced by an ether unit C-O-C,
 5 in a solvent or solvent mixture under basic to neutral conditions at a temperature of -20 to 120°C,
 which are subsequently reacted, in a solvent or solvent mixture under neutral to acidic conditions, with at least 2 equivalents of a compound of the formulae (IX),
 (X), (XI) or (XII)

10



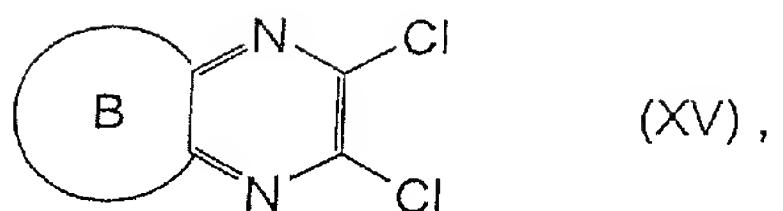
to give a further intermediate of the general formula (XIIIa) or (XIIIb)



15

from which subsequently one mole of ammonia or HOR_{12} is eliminated

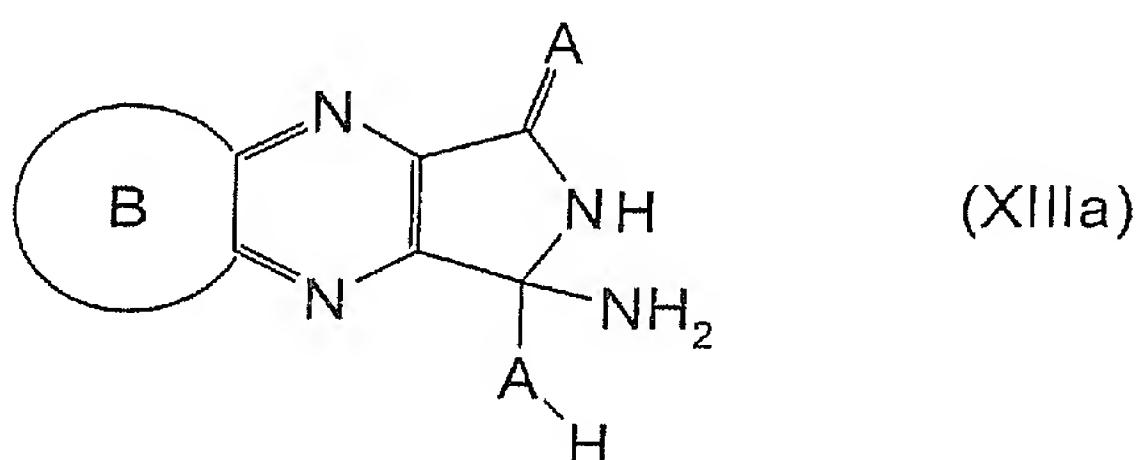
7. The process as claimed in claim 6, wherein the
 2,3-dicyanoquinoxaline is prepared by reacting 2,3-dichloroquinoxalines of the
 20 formula (XV)



with a cyanide of a main-group or transition-group metal in an organic solvent in the presence of a phase-transfer catalyst at elevated temperatures.

5

8. A compound of the general formula (XIIIa),



10 in which A and B are as defined in one or more of claims 1 to 5.

9. The use of a compound as claimed in one or more of claims 1 to 5 for dyeing or pigmenting organic or inorganic materials of high or low molecular weight.

15

10. The use as claimed in claim 9 as colorants in oil-based or water-based paints, in coating materials, camouflage paints, for spin coloring, for the mass coloring or pigmenting of plastics, in printing inks, in the mass coloring of paper, for seed, for preparing inks, water-based or non-water-based ink-jet inks,

20 microemulsion inks, and inks which operate in accordance with the hot-melt process.

11. The use as claimed in claim 9 as colorants for electrophotographic toners and developers, for color filters, for electronic inks, and for powder coating materials.

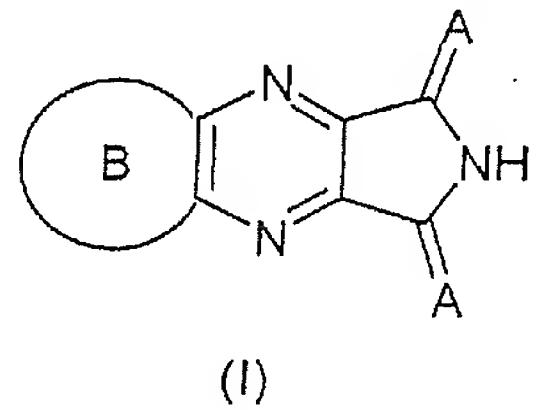
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12. A composition comprising an organic or inorganic, high or low molecular weight material and a compound as claimed in one or more of claims 1 to 5 in an amount of 0.005% to 70% by weight, based on the organic or inorganic material.

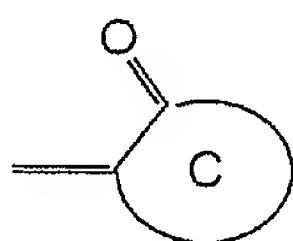
Abstract

Heterocyclic colorants based on diazabenzooisoindoles

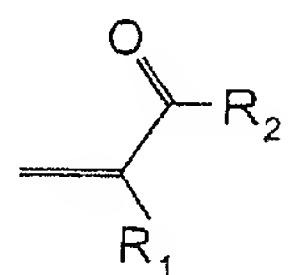
The invention relates to novel colorants of the formula (I)



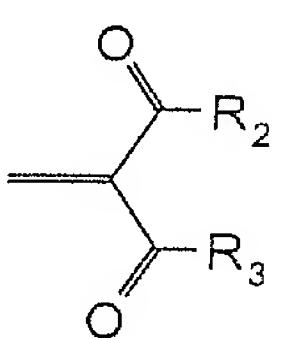
in which A is a group of the general formula (II), (III), (IV) or (V) and B is a substituted or unsubstituted ortho -C₆-C₁₈-arylene,



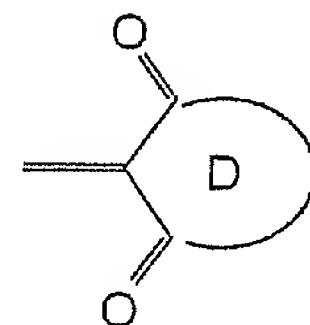
(II)



(III)



(IV)



(V)

in which C and D are an alicyclic or heterocyclic group.